Method for producing and controlling the morphology of metal-oxide nanofiber and/or nanotube catalysts.

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Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 November 2015 (12.11.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/169786 A1

(51) International Patent Classification:
D01D 1/02 (2006.01) *D01F 9/08* (2006.01)
D01D 5/00 (2006.01) *B82Y 30/00* (2011.01)
D01D 10/02 (2006.01)

(21) International Application Number:
PCT/EP2015/059807

(22) International Filing Date:
5 May 2015 (05.05.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
14167202.2 6 May 2014 (06.05.2014) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHOD FOR PRODUCING AND CONTROLLING THE MORPHOLOGY OF METAL-OXIDE NANOFIBER AND/OR NANOTUBE CATALYSTS

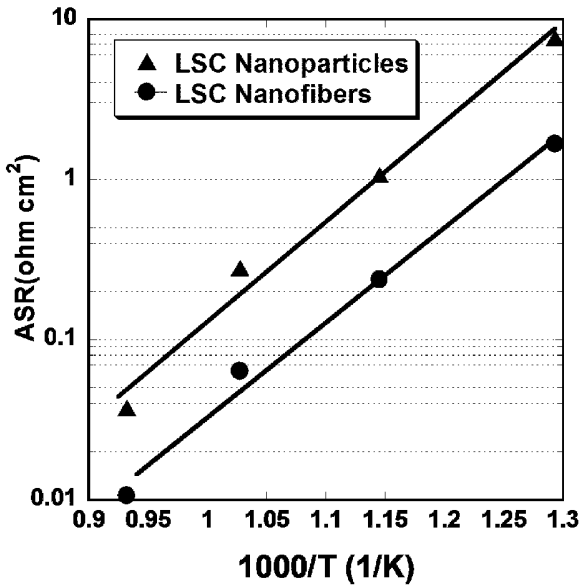


Fig. 2

(57) Abstract: Disclosed herein is a process for the controlled production of metal-containing nanofibers and/or nanotubes, where the morphology of the nanofibers and/or nanotubes is followed in real time by TEM measurements.

WO 2015/169786 A1

Published:

— *with international search report (Art. 21(3))*

Method for producing and controlling the morphology of Metal-Oxide Nanofiber and/or Nanotube Catalysts

The invention relates to a process for the controlled production of metal-containing nanofibers and/or nanotubes, where the morphology of the nanofibers and/or nanotubes is followed in real time.

Background

Metal-containing nanoparticles, nanofibers and/nanotubes are known to be good candidates as catalytic material, for use in electrochemical devices including fuel cells, water electrolysis and a number of other application purposes due to the high surface area which these materials have.

The efficiency of water electrolysis for example strongly depends on electrochemical behavior of electrodes and their structures. It is therefore important to develop materials which can enhance those characteristics. Perovskites are a group of metals which are promising and highly active electrocatalysts for the Oxygen Evolution Reaction (OER) in the alkaline media due to their many possible derivatives and electrical properties [Garcia, E.M., et al., International Journal of Hydrogen Energy, 2012, 37(8), p. 6400-6406].

Perovskite oxides of the type The $La_{1-x}Sr_xCoO_3$, where x is between 0-1, have for example been widely examined and are generally believed to have a positive effect on the oxygen evolution potential. As the performance of the electrodes strongly depends on the active surface area, it is important to synthesize materials with highly developed surface area.

One approach to synthesizing metal-containing nanofibers and/or nanotubes, e.g. of the Perovskite type, is to mix a solution containing a metal pre-cursor, and a solvent – possibly with the addition of a polymeric material – and electrospin this solution to obtain nanofibers and/or nanotubes, which may subsequently be calcinated or annealed to obtain the final product. Examples of such synthesis are shown in WO 2012/058425, EP 2 554 724, US 2012/0063058, US 8,512,741 and US 7,105,228.

A problem with all of the conventional methods for producing nanofibers/nanotubes described in these documents is that the morphology of the nanofibers/nanotubes may only be determined after the product has been synthesized. The optimum surface area for a specific application may therefore only be determined retrospectively.

Description of the invention

Disclosed herein is therefore a process for the production of metal-containing nanofibers and/or nanotubes. The process comprises a number of steps including a step of mixing

- a metal-containing pre-cursor mixture comprising one or more metal-containing pre-cursors;
- a polymer mixture comprising one or more polymers, and
- a solvent

to obtain a first mixture. The method further includes the steps of:

- electrospinning the first mixture to obtain polymer/metal-containing pre-cursor nanofibers;
- heating the polymer/ metal-containing pre-cursor nanofibers at temperatures between 300°C and 1500°C in a heating process, and
- monitoring the heating process by measuring multiple transmission electron microscopy (TEM) images of the polymer/metal-containing precursor nanofibers during the heating process as they are transformed into the metal-containing nanofibers and/or nanotubes, whereby the morphology of the metal-containing nanofibers and/or nanotubes is controlled by the monitoring of the heating process.

By the above is obtained a method where the morphology of the metal-containing nanofibers and/or nanotubes can be controlled both on the micro scale level but further on a nano scale level. This allows the user conducting the process to follow the heating process in real time and to further stop the process at exactly the time when the desired structure is obtained. Also the transition between nanofibers and nanotubes can be studied very precisely in real time, whereby the temperature at which the transition(s) occurs may be determined for each specific metal-containing

nanofibers and/or nanotubes depending on the metal used in the process and/or the solvent or polymer.

The heating process may advantageously by an *in-situ* sintering process. In conventional processes a calcination or an annealing process normally occurs.

Calcination is a thermal treatment usually used for synthesis of a powder samples. It involves decomposition, phase transition and evaporation of volatile components. The process usually progress in presence of air or oxygen applied to ores and other solid materials to bring about the thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials.

Annealing is a heat treatment that alters a material to increase its ductility and to make it more workable. It involves heating a material to above its critical temperature, maintaining a suitable temperature, and then cooling. Annealing can induce ductility, soften material, relieve internal stresses, refine the structure by making it homogeneous, and improve cold working properties.

Sintering on the other hand is used to create a subject from a powder with a certain shape (e.g., pallet, thin film, membranes), where the sample is heated to a temperature below the melting point. Sintering involves atom diffusion, which results in particle fusion. The sintering process allows for control of the grain size as well as the final morphology (nanofiber or nanotubes), which is highly advantageous in combination with the use of TEM imaging to monitor the process in details in real time.

Disclosed herein is also a metal-containing nanofibers and/or nanotubes produced by a process according to the above.

Disclosed herein is further the use of a metal-containing nanofibers and/or nanotubes produced by the method disclosed above as:

- a catalyst;
- a catalyst in water electrolysis;

- a material in solid oxide fuel cells (SOFC);
- a material in regenerative fuel cells;
- a material in lithium-air batteries;
- a material in thermal-electrical devices;
- a material in magnetic cooling devices;
- a material in flue gas purification devices;
- a material in oxygen membranes;
- a material in liquid/gas filtrations;
- a material in gas storage devices, or
- a material in electrochemical pseudo capacitors.

Brief description of the drawings

Figure 1 shows a schematic overview of a process for the production of metal-containing nanofibers and/or nanotubes according to th invention.

Figure 2 shows the polarization resistance, R_p, as a function of the reciprocal absolute temperature for LSC nanoparticles and LSC nanofibers in a symmetric cell tests. The activation energies are also indicated. The trend line for the determination of the activation energy of the experimentally derived Rp is indicated by a line.

Figure 3 shows the evolution of resistance as a function of the thickness of the column of powder for LSC nanoparticles and LSC nanofibers.

Figure 4 shows the relative dependence of performance of LSC nanoparticles and LSC nanofibers towards the OER in 1M KOH at room temperature, 1200 rpm.

Figure 5 shows the Tafel slopes for LSC nanoparticles and LSC nanofibers for the OER in 1M KOH at room temperature, 1200 rpm.

Figure 6 shows selected TEM images of single nanofibers sintered in an in-situ TEM while temperature was increased from 30°C to 1000°C.

Description of preferred embodiments

In the following embodiments of the invention will be described in further details with reference to the figures, where figure 1 shows a flow diagram representing the process for the production of metal-containing nanofibers and/or nanotubes.

The process comprises a series of steps, where the first step 101 is the mixing of 1) a metal-containing pre-cursor mixture comprising one or more metal-containing pre-cursors, 2) a polymer mixture comprising one or more polymers, and 3) a solvent to obtain a first mixture.

In one or more embodiments the metal-containing pre-cursor mixture and the solvent are mixed before adding the polymer mixture.

In one or more embodiments the one or more metal-containing pre-cursors is selected from acetate salts, iso-propoxide salts, chloride salt, or nitrate salts. The salts may comprise a metal from the group of lanthanum (La), strontium (Sr), scandium (Sc), yttrium (Y), cobalt (Co), iron (Fe), zinc (Zn), cerium (Ce), gadolinium (Gd), manganese (Mn), zirconium (Zr), barium (Ba), nickel (Ni), tin (Sn), silicon (Si), vanadium (V), tungsten (W), lithium (Li), titanium (Ti), germanium (Ge), antimony (Sb), aluminium (Al), chrome (Cr), calcium (Ca), sodium (Na), silver (Ag), gold (Au), platinum (Pt) and molybdenum (Mo).

In one or more embodiments the one or more polymer is selected from the group of polyvinylpyrrolidone, polyethylene oxide, poly acrylic acid, polyacrylonitrile polyvinyl alcohol, polyvinyl acetate, polymethyl methacrylate, polybenzimidazole or a mixture of two or more of these polymers.

In one or more embodiments the solvent is selected from the group of water, alcohol, isopropanol, dimethylformamide (DMF), dimethylacetamide (DMAc), acetate acid, and acetone.

The second step 102 of the process shown in figure 1 is an electrospinning of the first mixture to obtain polymer/metal-containing pre-cursor nanofibers, which is followed by a combined and real time heating/monitoring step 103, where the

polymer/metal-containing pre-cursor nanofibers are heated at temperatures between 300°C and 1500°C.

During the heating process 104, multiple transmission electron microscopy (TEM) images of the polymer/metal-containing precursor nanofibers are obtained 105 as they are transformed into the metal-containing nanofibers and/or nanotubes. The TEM images are obtained directly on the sample as it is heated, e.g. it is an on-site process. Continuously obtaining TEM images allows for a direct control of the morphology of the metal-containing nanofibers and/or nanotubes.

In one or more embodiments the heating temperature is between 350°C and 1200°C, or between 350°C and 1000°C, or between 400°C and 800°C, or between 350°C and 700°C.

In one or more embodiments the temperature in the heating process reaches a starting temperature, the heating temperature is increased with a ramping rate of between 0.5°C/min and 20°C/min while TEM spectra are recorded simultaneously with increasing the temperature. Alternatively, the ramping rate may be between 2° C/min and 15°C/min, or between 5° C/min and 15°C/min, or between 0.5° C/min and 5°C/min, or between 15° C/min and 20°C/min, or between 10° C/min and 15°C/min.

In one or more embodiments the heating process is an *in-situ* sintering process occurring in the presence of air, a gas mixture containing oxygen or pure oxygen.

In the last step 106 in figure 1, the heating process 104 is stopped when the desired morphology of the metal-containing nanofibers and/or nanotubes is obtained.

In one or more embodiments controlling the morphology of the metal-containing nanofibers and/or nanotubes are obtained by stopping the heating process when the metal-containing nanofibers and/or nanotubes takes the form of a nanofiber or a hollow nanotube depending on which choice is the preferred by the user, wherein stopping the heating process is done by decreasing the temperature.

In one or more embodiments controlling the morphology of the metal-containing nanofibers and/or nanotubes are obtained by stopping the heating process when a predetermined grain size of the metal-containing nanoparticles in the metal-containing nanofibers and/or nanotubes are obtained, wherein stopping the heating process is done by decreasing the temperature.

In one or more embodiments controlling the morphology of the metal-containing nanofibers and/or nanotubes are obtained by stopping the heating process when a predetermined diameter of the metal-containing nanofibers is obtained, wherein stopping the heating process is done by decreasing the temperature.

In one or more embodiments controlling the morphology of the metal-containing nanofibers and/or nanotubes are obtained by stopping the heating process when a predetermined diameter of the metal-containing nanotubes is obtained, wherein stopping the heating process is done by decreasing the temperature.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may have a morphology of the metal-containing nanofibers and/or nanotubes which changes from nanofibers to nanotubes at a first temperature range between 300°C and 400°C and/or from nanotubes to nanofibers at a second temperature range between 700°C and 900°C.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are metal nanofibers and/or nanotubes.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are silver or platinum nanofibers and/or nanotubes.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are metal oxide nanofibers and/or nanotubes.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are zirconium oxide if the metal-containing pre-cursor is zirconium acetate, zirconium iso-propoxide, zirconium chloride, or zirconium nitrate.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are cerium oxide if the metal-containing pre-cursor is cerium acetate, cerium iso-propoxide, cerium chloride or cerium nitrate.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are nickel oxide if the metal-containing pre-cursor is nickel acetate, nickel iso-propoxide, nickel chloride or nickel nitrate.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are zinc oxide if the metal-containing pre-cursor is zinc acetate, zinc iso-propoxide, zinc chloride or zinc nitrate.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are calcium oxide if the metal-containing pre-cursor is calcium acetate, calcium iso-propoxide, calcium chloride or calcium nitrate.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are strontium sodium silicon oxide (SNS) if the metal-containing pre-cursor mixture comprises a mixture of:

- sodium acetate, sodium iso-propoxide, sodium chloride or sodium nitrate;
- strontium acetate, strontium iso-propoxide, strontium chloride or strontium nitrate, and
- tetramethyl orthosilicate or silicon dioxide.

In one or more embodiments the produced metal-containing nanofibers and/or nanotubes are Perovskite oxide nanofibers and/or nanotubes.

In one or more embodiments the produced Perovskite oxide nanofibers and/or nanotubes is lanthanum strontium cobalt ferrite (LSCF) oxide if the metal-containing pre-cursor mixture comprises:

- lanthanum acetate, lanthanum iso-propoxide, lanthanum chloride or lanthanum nitrate;

- strontium acetate, strontium iso-propoxide, strontium chloride or strontium nitrate;
- cobalt acetate, cobalt iso-propoxide, cobalt chloride or cobalt nitrate, and
- iron acetate, iron iso-propoxide, iron chloride or iron nitrate.

In one or more embodiments the produced Perowskite oxide nanofibers and/or nanotubes is lanthanum strontium cobalt (LSC) oxide if the metal-containing pre-cursor mixture comprises:

- lanthanum acetate, lanthanum iso-propoxide, lanthanum chloride or lanthanum nitrate;
- strontium acetate, strontium iso-propoxide, strontium chloride or strontium nitrate, and
- cobalt acetate, cobalt iso-propoxide, cobalt chloride or cobalt nitrate.

In one or more embodiments lanthanum (La), strontium (Sr), cobalt (Co), and oxide (O) in LSC is distributed in the ratio of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$, where δ is a number between 0-3. This includes both integers between 0 and 3 and non-integers.

In one or more embodiments the produced Perowskite oxide nanofibers and/or nanotubes is lanthanum strontium manganite (LSM) oxide if the metal-containing pre-cursor mixture comprises:

- lanthanum acetate, lanthanum iso-propoxide, lanthanum chloride or lanthanum nitrate;
- strontium acetate, strontium iso-propoxide, strontium chloride or strontium nitrate, and
- manganese acetate, manganese iso-propoxide, manganese chloride or manganese nitrate.

In one or more embodiments the produced Perowskite oxide nanofibers and/or nanotubes is eria gadolinium oxide (CGO) if the metal-containing pre-cursor mixture comprises:

- cerium acetate, cerium iso-propoxide, cerium chloride or cerium nitrate, and
- gadolinium acetate, gadolinium iso-propoxide, gadolinium chloride or gadolinium nitrate.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a catalyst.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a catalyst in water electrolysis.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in solid oxide fuel cells (SOFC).

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in regenerative fuel cells.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in lithium-air batteries.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in thermal-electrical devices.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in magnetic cooling devices.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in flue gas purification devices.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in oxygen membranes.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in liquid/gas filtrations.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in gas storage devices.

The metal-containing nanofibers and/or nanotubes produced by the method disclosed herein may in one or more embodiments by used as a material in electrochemical pseudo capacitors.

Symmetric cell test (for applications in SOFC)

Figure 2 shows the measured cathode polarization resistance R_p plotted against inverse absolute temperature for both a LSC nanoparticle cathode and LSC nanofiber cathode in a symmetric cell tests. The activation energies are also indicated. The trend line for the determination of the activation energy of the experimentally derived Rp is indicated by a line. The results are summarized in Table 1.

Table 1: *Symmetric cell tests for LSC nanoparticle and nanofiber cathode*

		LSC Nanoparticles	LSC Nanofiber
Cathode Polarization Resistance	**500 °C**	**7.64 Ω·cm^2**	**1.66 Ω·cm^2**
	600 °C	**1.06 Ω·cm^2**	**0.23 Ω·cm^2**
	700 °C	**0.28 Ω·cm^2**	**0.063 Ω·cm^2**
	800 °C	**0.037 Ω·cm^2**	**0.01 Ω·cm^2**
Activation Energy		1.22 eV	1.19 eV

In general the cathode polarization resistance (R_p) for both the LSC nanofiber cathode and the LSC nanoparticle cathode increases when the operating

temperature decreases as can be seen in figure 2 and Table 1. However, the LSC nanofiber cathode shows relatively lower R_p for all temperature range compared to the LSC nanoparticle cathode.

At 600°C, the LSC nanofiber cathode has an R_p of 0.23 $\Omega \cdot cm^2$, which represents a 78% reduction compared to the cathode made of LSC nanoparticles. The relatively lower activation energy is also observed for LSC nanofiber cathode, indicating a highly effective cathode structure or a larger catalytic surface area that is available for the reaction.

Tests for Alkaline Electrolysis System

Figure 3 shows the conductivity measured in a cell for LSC nanoparticles and LSC nanofibers. As experiments are performed on the thin coating consisting of an electrocatalyst and a binder, it is important to make sure that coating is preserved after the electrochemical tests.

To evaluate the electrochemical performance towards the OER, a polarization curve is obtained and shown in figure 4. As can be seen in figure 4, the activity of LSC nanofibers is much higher than that of the powdered LSC.

To compare the relative performance of two materials, the onset current densities is measured at 690 mV for the OER, which corresponded to 17 mA/mg and 46 mA/mg for the LSC nanoparticles and LSC nanofibers, respectively, at 1200 RPM.

To determine the mechanism of the OER on the LSC surfaces, a Tafel plot as shown in figure 5 is recorded. From figure 5 it can be seen that the exchange current densities are higher than for LSC nanoparticles. The measured inclines of the Tafel slopes are 62 and 70 mV/dec for LSC nanoparticles and LSC nanofibers, respectively.

Figure 6 shows the TEM images of the single nanofiber at varied sintering temperature from. From 36°C to 350°C, the diameter of the nanofiber decreases with temperature due to the degradation of PVP component. When temperature increases further, the sintering of ceramic nanoparticles takes place. The nanofiber

changes to a nanotube composing of very fine nanoparticles. As temperature goes up to 790°C, the nanoparticles grow with bigger grain size. Another transition from nanofiber to nanotube takes place again at temperature of 890°C. The diameter of the grain grows further from ~80nm to ~200nm.

Experimental Details

Synthesis of LSC Nanofibers

$La(NO_3)\cdot 6H_2O$, $Sr(NO_3)_2$ and $Co(NO_3)_3\cdot 6H_2O$ are dissolved in de-ionized water at a molar ratio of 0.6:0.4:1 in order to synthesis $(La_{0.6}Sr_{0.4})_{0.99}CoO_3$. The solution is stirred at 60°C until complete dissolution. Polyvinylpyrrolidone (PVP) is used as carrier polymer and a desired amount of PVP powder is added to the above solution. The weight ratio of PVP powder to nitrate salts is set as 0.4. The solution is stirred at 60°C until a clear pink solution is formed.

If a higher ratio of PVP over nitrate salt is used, the result will be finer LSC nanofibers due to the higher concentration of PVP content. Likewise, a lower ratio of PVP results in electrosprayed droplets instead of nanofibers.

The resultant precursor is then loaded into a 10ml syringe with a 21 gauge stainless steel needle attached to the tip of the syringe. The syringe is then mounted on a syringe pump. During electrospinning, the precursor is pumped out of the needle at an injection rate of 0.3 ml/h with an electrical field of 4.4 kV/cm. A grounded aluminium foil is used as a collector to collect the electrospun nanofibers. The as-spun nanofiber membrane is then peeled off from the foil and then sintered in a furnace under an atmosphere of air. The sintering profile is carefully designed to achieve both Perovskite phase as well as desired nano-morphological features of LSC nanofibers.

The sintering behaviour of single nanofibers with increase of temperature is studied by in-situ TEM (FEI Titan E-Cell 80-300 ST TEM). The temperature is increased from 30°C to 900°C with the heating rate of 5°C/min. The gas in the chamber of the TEM is N2 with 0.2 % O_2. All TEM images are taken on the same nanofiber.

LSC nanofiber cathode for Solid Oxide Fuel Cells (SOFC's)

Both LSC nanofibers and LSC nanoparticles are tested in a symmetric cell. The center of symmetric cells consists of a dense ceria gadolinium oxide (CGO) electrolyte doped with 1wt% Co. The cell has a pallet with a diameter of 10mm and a thickness of 2mm. To enhance the adhesion between the LSC nanofibers and/or nanoparticles and the CGO electrolyte, a thin layer of electrospinning precursor (described in preceding section relating to the synthesis of LSC nanofibers) is brushed on both sides of CGO pallet followed by drying at 80°C until a polymer thin film is formed.

For a symmetric cell with a LSC nanofiber as cathode, the LSC nanofiber membrane (after sintering) is first grounded in the solvent of Dowanol to create a LSC nanofiber paste. The paste is then brushed on both sides of CGO pallet, which is covered by thin films of precursor material. A CGO electrolyte sandwiched by LSC nanofiber cathodes is formed after sintering at 750°C in air for 1 hour. For comparison, the same method may also be used to prepare a CGO electrolyte sandwiched by LSC nanoparticles cathodes. In all cases, Pt paste and a Pt mesh are used for current collection of the symmetric cells.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy is carried out using a Solartron 1260 impedance analyzer with a frequency range from 0.01 Hz to 100 kHz. The samples are tested with a 50mV amplitude AC signal under open-circuit conditions. The data are normalized with the measured geometrical area of the pallet (around 0.785 cm^2) and are divided by 2 to account for the symmetric structure of the cells. The data is corrected for the series inductance of the measurement rig determined by measuring the set-up without any samples.

LSC nanofiber electrocatalysts for Alkaline Electrolysis Cells

All experiments are performed in 1M KOH at room temperature using a rotating disk electrode (3600 RPM). A three-electrode glass cell and the RDE shaft are provided by Radiometer analytical. To study the activity of the electrocatalysts towards the Oxygen Evolution Reaction (OER), a 0.3 to 0.73 V vs. Hg/HgO reference electrode is used. All scans are performed at 1 mV/s using rotation rates of 3600, 2400, 1200,

600 and 300 RPM consequently. The electrodes are prepared by drop wise application of the catalyst ink on the polished surface of the RDE tips.

Preparation of reasonably stable dispersion of oxide powder may be a delicate procedure, which requires choice of proper solvent, amount of electrocatalyst and electrode surface preparation. In this work, the working glassy carbon electrode is 5 mm in diameter and consists of the drop-casted thin electrocatalyst film. The surface of the Glassy carbon electrode is polished with spray containing 0.5 µm diamond powder ("DP-Spray" provided by Struers A/S), rinsed with de-mineralized water several times and dried with the dry tissue.

The catalyst ink is prepared as following: 1.5 mg of electrocatalyst is dissolved in 300 µl of isopropanol and 24 µl of binder to create a homogeneous ink. Binder consisted of a pH7-stabilized 5 wt.% commercial solution of Nafion® (by DuPont) using KOH and Isopropanol is used. Dispersion is ultrasonicated for 1 hour before application on the electrode, following drying at room temperature until the dense foil is formed on the surface of the electrode. Hg/HgO reference electrode is provided by Radiometer Analytical and all measurements are performed at Nitrogen-saturated solution with 30 minutes purging prior to each experiment.

In order to characterize the relative activity of the electrodes, a conventional Rotating Disk Electrode was used. The electrochemical behavior was evaluated by voltammetrics and the Tafel extrapolations in 1M KOH.

Claims

1. A process for the production of metal-containing nanofibers and/or nanotubes, the process comprising the steps of:

- mixing
  - a metal-containing pre-cursor mixture comprising one or more metal-containing pre-cursors;
  - a polymer mixture comprising one or more polymers, and
  - a solvent

  to obtain a first mixture;
- electrospinning the first mixture to obtain polymer/metal-containing pre-cursor nanofibers;
- heating the polymer/ metal-containing pre-cursor nanofibers at temperatures between 300°C and 1500°C in a heating process, and
- monitoring the heating process by measuring multiple transmission electron microscopy (TEM) images of the polymer/metal-containing precursor nanofibers during the heating process as they are transformed into the metal-containing nanofibers and/or nanotubes, whereby the morphology of the metal-containing nanofibers and/or nanotubes is controlled by the monitoring of the heating process.

2. A process according to claim 1, wherein the heating process is an *in-situ* sintering process.

3. A process according to any preceding claim, wherein controlling the morphology of the metal-containing nanofibers and/or nanotubes are obtained by stopping the heating process when:

- the metal-containing nanofibers and/or nanotubes takes the form of a nanofiber or a hollow nanotube depending on which choice is the preferred by the user, and/or
- a predetermined grain size of the metal-containing nanoparticles in the metal-containing nanofibers and/or nanotubes are obtained, and/or
- a predetermined diameter of the metal-containing nanofibers is obtained, and/or

- a predetermined diameter of the metal-containing nanotubes is obtained,

wherein stopping the heating process is done by decreasing the temperature.

4. A process according to any preceding claim, wherein the one or more metal-containing pre-cursors is selected from:
   - acetate salts;
   - iso-propoxide salts;
   - chloride salt, or nitrate salts,

   wherein the salts comprises a metal from the group of lanthanum (La), strontium (Sr), scandium (Sc), yttrium (Y), cobalt (Co), iron (Fe), zinc (Zn), cerium (Ce), gadolinium (Gd), manganese (Mn), zirconium (Zr), barium (Ba), nickel (Ni), tin (Sn), silicon (Si), vanadium (V), tungsten (W), lithium (Li), titanium (Ti), germanium (Ge), antimony (Sb), aluminium (Al), chrome (Cr), calcium (Ca), sodium (Na), silver (Ag), platinum (Pt), gold (Au) and molybdenum (Mo).

5. A process according to any preceding claim, wherein the produced metal-containing nanofibers and/or nanotubes are:
   - metal nanofibers and/or nanotubes, e.g. silver or platinum nanofibers and/or nanotubes;
   - metal oxide nanofibers and/or nanotubes, or
   - Perovskite oxide nanofibers and/or nanotubes.

6. A process according to any preceding claim, wherein the produced metal-containing nanofibers and/or nanotubes are metal oxide nanofibers and/or nanotubes of the type:
   - zirconium oxide if the metal-containing pre-cursor is zirconium acetate, zirconium iso-propoxide, zirconium chloride, or zirconium nitrate,
   - cerium oxide if the metal-containing pre-cursor is cerium acetate, cerium iso-propoxide, cerium chloride or cerium nitrate,
   - nickel oxide if the metal-containing pre-cursor is nickel acetate, nickel iso-propoxide, nickel chloride or nickel nitrate,

- zinc oxide if the metal-containing pre-cursor is zinc acetate, zinc iso-propoxide, zinc chloride or zinc nitrate,
- calcium oxide if the metal-containing pre-cursor is calcium acetate, calcium iso-propoxide, calcium chloride or calcium nitrate, or
- strontium sodium silicon oxide (SNS) if the metal-containing pre-cursor mixture comprises a mixture of:
  - sodium acetate, sodium iso-propoxide, sodium chloride or sodium nitrate;
  - strontium acetate, strontium iso-propoxide, strontium chloride or strontium nitrate, and
  - tetramethyl orthosilicate or silicon dioxide.

7. A process according to any of the claims 1-5, wherein the produced metal-containing nanofibers and/or nanotubes are the produced Perovskite oxide nanofibers and/or nanotubes of the type:
   - lanthanum strontium cobalt ferrite (LSCF) oxide if the metal-containing pre-cursor mixture comprises:
     - lanthanum acetate, lanthanum iso-propoxide, lanthanum chloride or lanthanum nitrate;
     - strontium acetate, strontium iso-propoxide, strontium chloride or strontium nitrate;
     - cobalt acetate, cobalt iso-propoxide, cobalt chloride or cobalt nitrate, and
     - iron acetate, iron iso-propoxide, iron chloride or iron nitrate,
   - lanthanum strontium cobalt (LSC) oxide if the metal-containing pre-cursor mixture comprises:
     - lanthanum acetate, lanthanum iso-propoxide, lanthanum chloride or lanthanum nitrate;
     - strontium acetate, strontium iso-propoxide, strontium chloride or strontium nitrate, and
     - cobalt acetate, cobalt iso-propoxide, cobalt chloride or cobalt nitrate,
   - lanthanum strontium manganite (LSM) oxide if the metal-containing pre-cursor mixture comprises:

- lanthanum acetate, lanthanum iso-propoxide, lanthanum chloride or lanthanum nitrate;
- strontium acetate, strontium iso-propoxide, strontium chloride or strontium nitrate, and
- manganese acetate, manganese iso-propoxide, manganese chloride or manganese nitrate, or

- ceria gadolinium oxide (CGO) if the metal-containing pre-cursor mixture comprises:
  - cerium acetate, cerium iso-propoxide, cerium chloride or cerium nitrate, and
  - gadolinium acetate, gadolinium iso-propoxide, gadolinium chloride or gadolinium nitrate.

8. A process according to claim 7, wherein lanthanum (La), strontium (Sr), cobalt (Co), and oxide (O) in LSC is distributed in the ratio of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$, where δ is between 0 and 3.

9. A process according to any preceding claim, wherein the one or more polymer is selected from the group of polyvinylpyrrolidone, polyethylene oxide, poly acrylic acid, polyacrylonitrile polyvinyl alcohol, polyvinyl acetate, polymethyl methacrylate, polybenzimidazole or a mixture of two or more of these polymers.

10. A process according to any preceding claim, wherein the solvent is selected from the group of water, alcohol, isopropanol, dimethylformamide (DMF), dimethylacetamide (DMAc), acetate acid, and acetone.

11. A process according to any preceding claim, wherein the heating temperature is between 350°C and 1200°C, or between 350°C and 1000°C, or between 400°C and 800°C, or between 350°C and 700°C.

12. A process according to any preceding claim, wherein the heating process is an *in-situ* sintering process occurring in the presence of air, a gas mixture containing oxygen or pure oxygen.

13. Metal-containing nanofibers and/or nanotubes produced by a process according to any of claims 1-12.

14. Metal-containing nanofibers and/or nanotubes according to claim 13, wherein the morphology of the metal-containing nanofibers and/or nanotubes changes from nanofibers to nanotubes at a first temperature range between 300°C and 400°C and/or from nanotubes to nanofibers at a second temperature range between 700°C and 900°C.

15. Use of metal-containing nanofibers and/or nanotubes produced by a process according to any of claims 1-12 as:

- a catalyst;
- a catalyst in water electrolysis;
- a material in solid oxide fuel cells (SOFC);
- a material in regenerative fuel cells;
- a material in lithium-air batteries;
- a material in thermal-electrical devices;
- a material in magnetic cooling devices;
- a material in flue gas purification devices;
- a material in oxygen membranes;
- a material in liquid/gas filtrations;
- a material in gas storage devices, or
- a material in electrochemical pseudo capacitors.

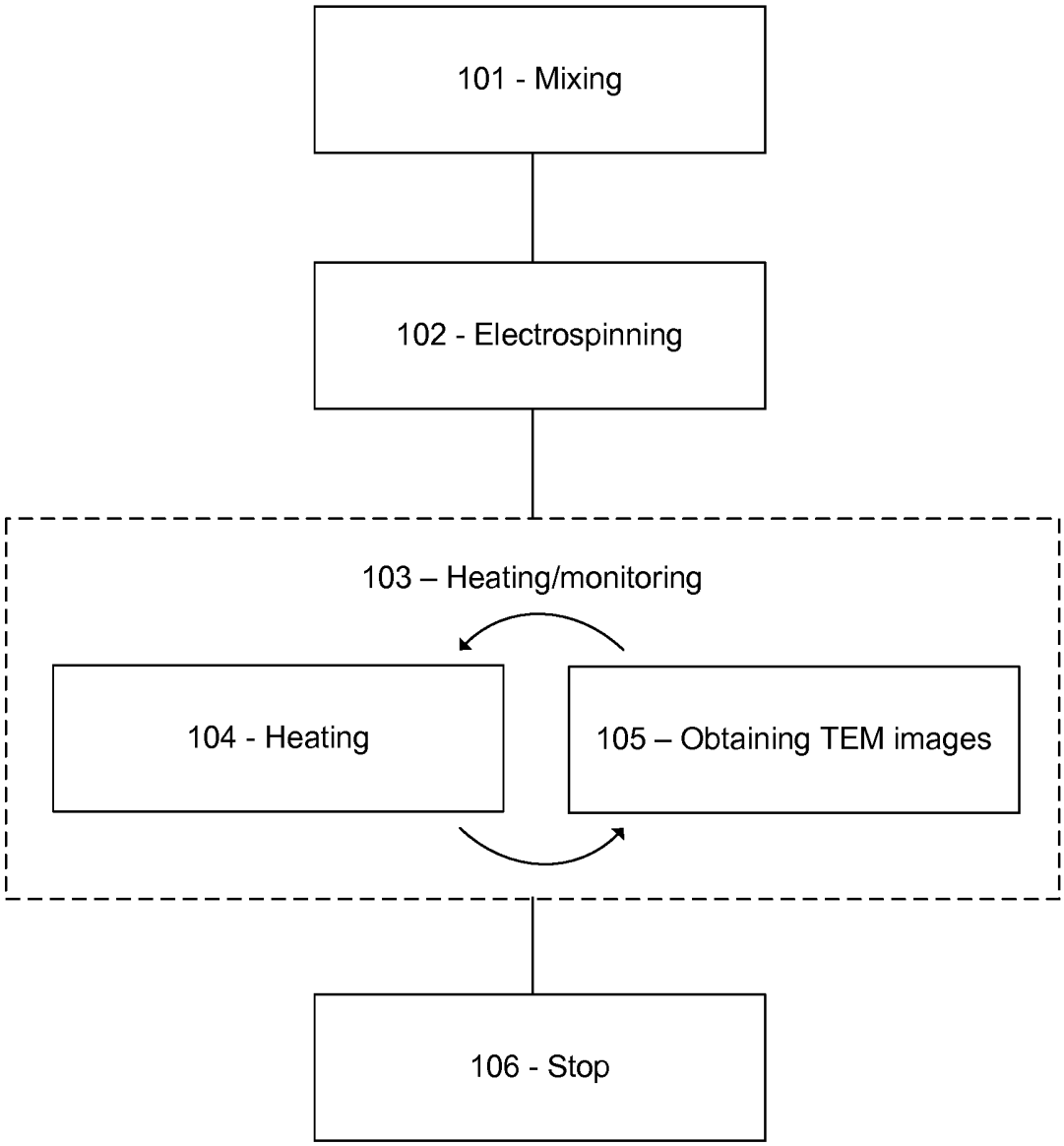

101 - Mixing
102 - Electrospinning
103 – Heating/monitoring
104 - Heating
105 – Obtaining TEM images
106 - Stop

Fig. 1

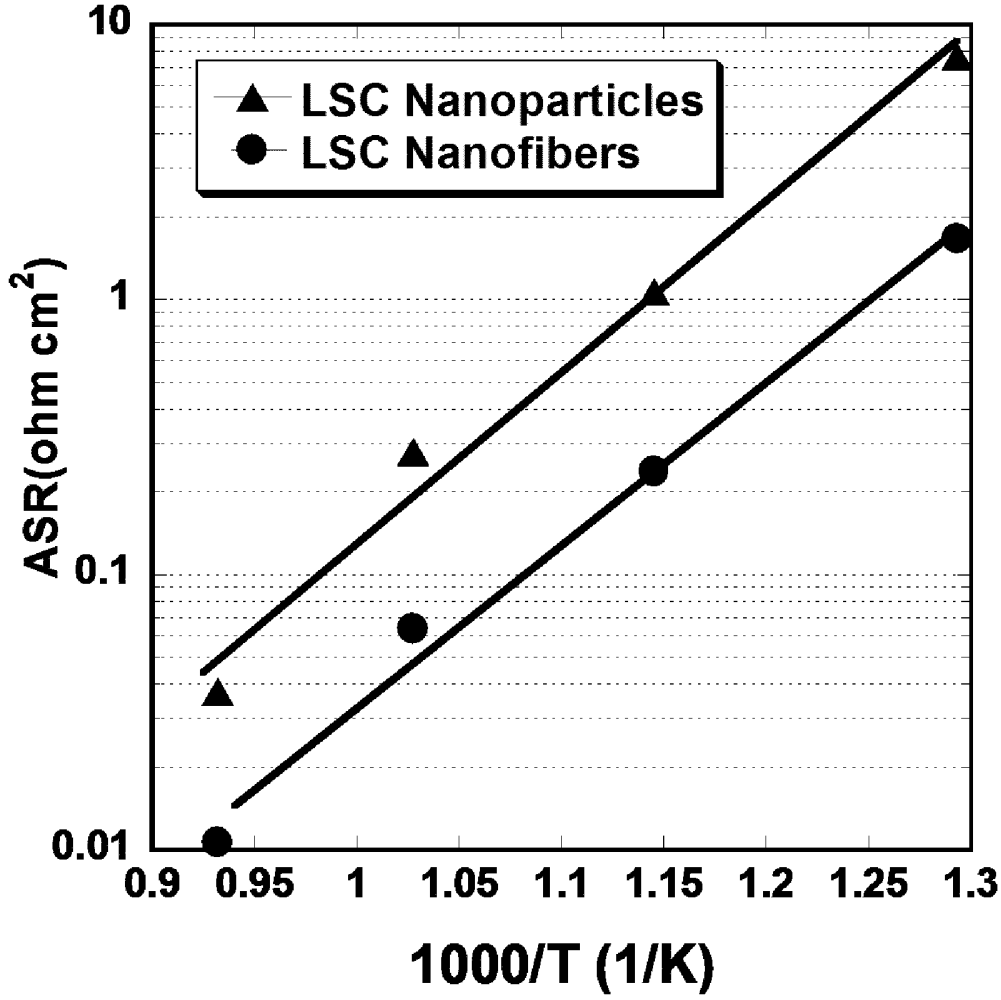

10
1
0.1
0.01
ASR(ohm cm2)
LSC Nanoparticles
LSC Nanofibers
0.9
0.95
1
1.05
1.1
1.15
1.2
1.25
1.3
1000/T (1/K)

Fig. 2

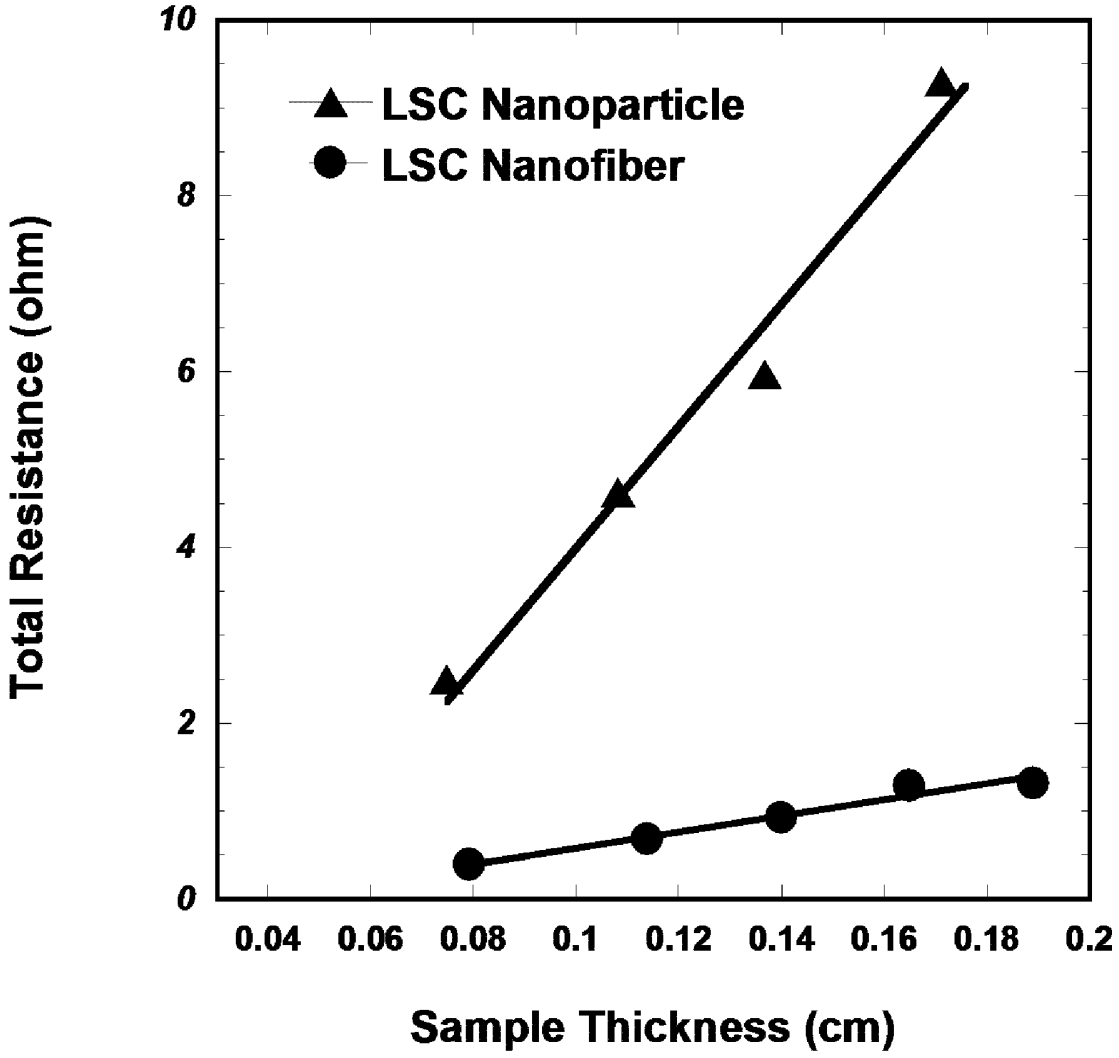
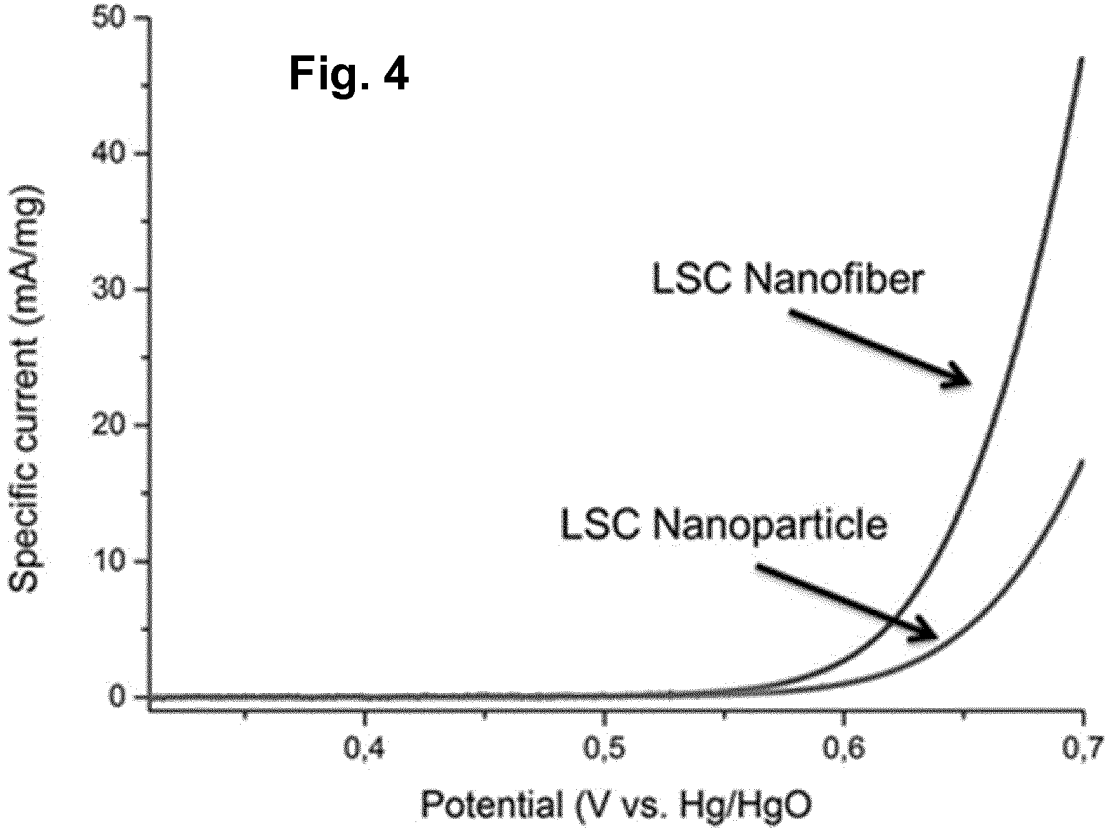

LSC Nanoparticle
LSC Nanofiber
Total Resistance (ohm)
Sample Thickness (cm)
0
2
4
6
8
10
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2

Fig. 3

Fig. 4


50
40
30
20
10
0
Specific current (mA/mg)
LSC Nanofiber
LSC Nanoparticle
0,4
0,5
0,6
0,7
Potential (V vs. Hg/HgO

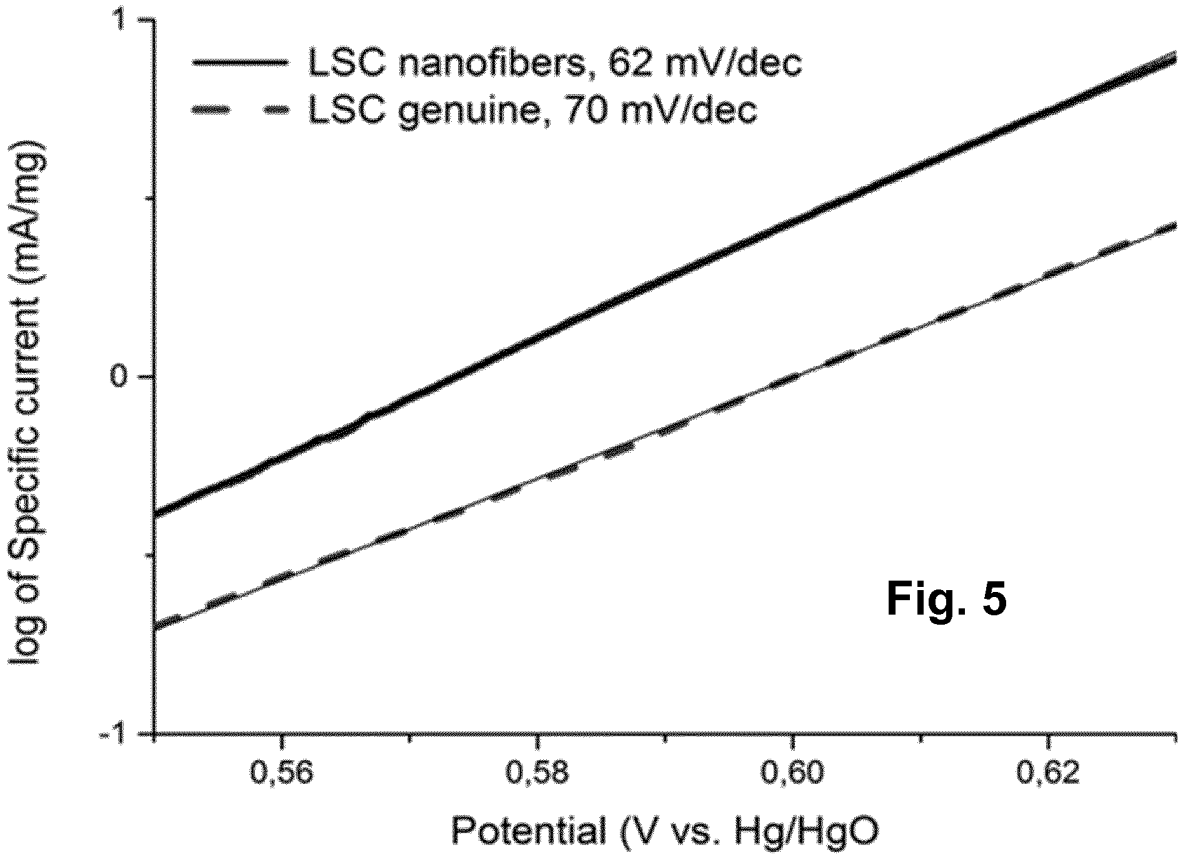

1
0
-1
log of Specific current (mA/mg)
LSC nanofibers, 62 mV/dec
LSC genuine, 70 mV/dec
0,56
0,58
0,60
0,62
Potential (V vs. Hg/HgO

Fig. 5

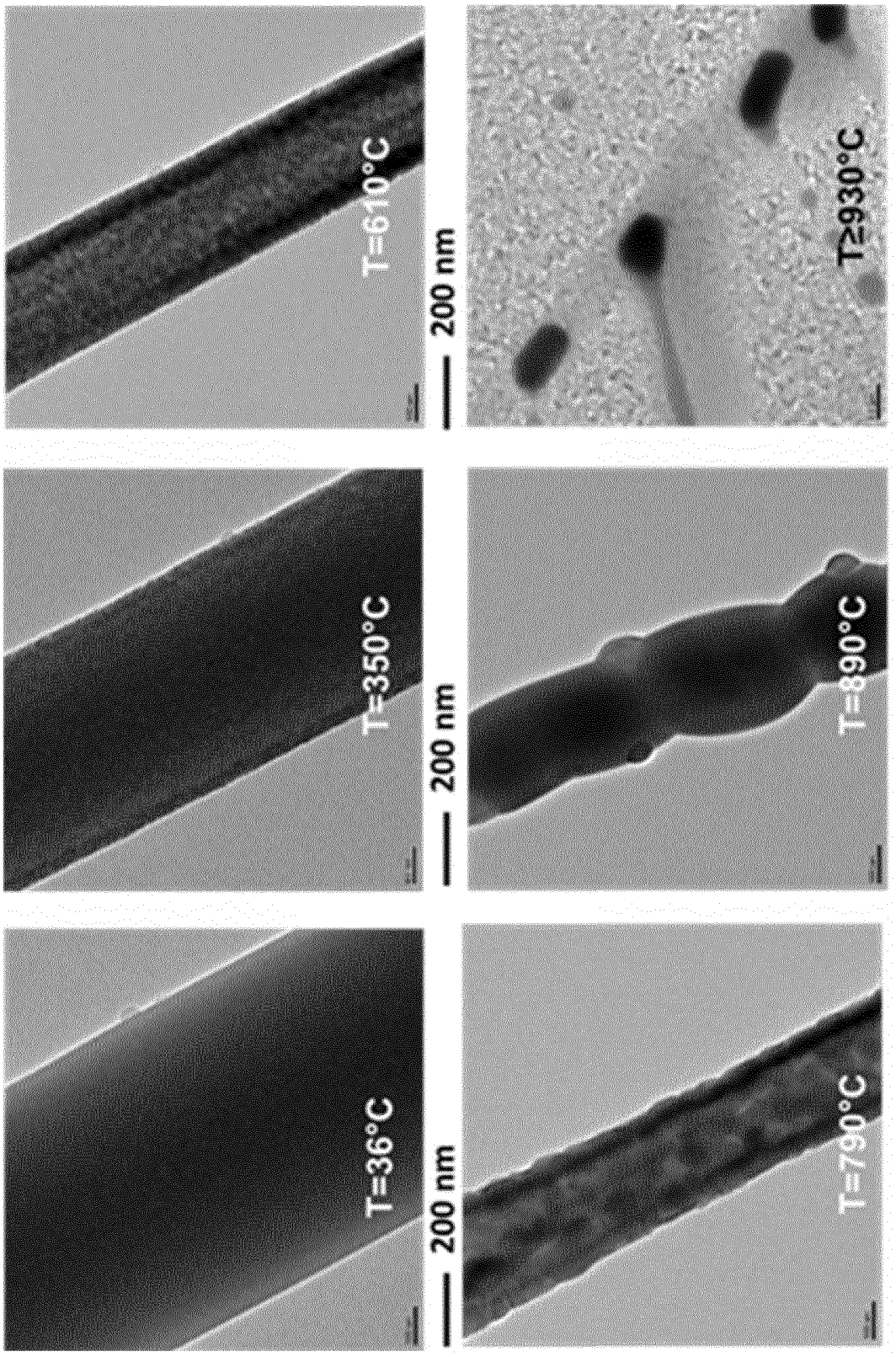


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/059807

A. CLASSIFICATION OF SUBJECT MATTER
INV. D01D1/02 D01D5/00 D01D10/02 D01F9/08 B82Y30/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D01D D01F B82Y C04B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DHARMARAJ N ET AL: "Preparation and morphology of magnesium titanate nanofibres via electrospinning", INORGANIC CHEMISTRY COMMUNICATIONS, ELSEVIER, AMSTERDAM, NL, vol. 7, no. 3, 1 March 2004 (2004-03-01), pages 431-433, XP027535996, ISSN: 1387-7003 [retrieved on 2004-02-17]	13-15
A	the whole document	1-12

X	US 2008/305377 A1 (SHUI JIANGLAN [US] ET AL) 11 December 2008 (2008-12-11)	13-15
A	abstract; figures 3-6,9,10; examples 2,3	1-12

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 July 2015	28/07/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Malik, Jan

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/059807

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ABDUL-MAJEED AZAD ET AL: "Processing and characterization of electrospun Y2O3-stabilized ZrO2 (YSZ) and Gd2O3-doped CeO2 (GDC) nanofibers", MATERIALS SCIENCE AND ENGINEERING B, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 123, no. 3, 25 November 2005 (2005-11-25), pages 252-258, XP002713279, ISSN: 0921-5107, DOI: 10.1016/J.MSEB.2005.08.070 the whole document	13-15

X	WO 2010/120964 A2 (UNIV DELAWARE [US]; CHEN XING [US]; XIAO JOHN Q [US]; SUN ZAICHENG [US) 21 October 2010 (2010-10-21)	13-15
A	abstract; claims 8-14,21,23,35,37,38; figure 1	1-12

X	EP 2 204 349 A1 (KOREA INST SCI & TECH [KR]) 7 July 2010 (2010-07-07) paragraphs [0005], [0025] - [0034], [0036]; examples 1-5	13,14

X	EP 2 554 724 A9 (UNIV TSINGHUA [CN]; TOYOTA MOTOR CO LTD [JP]) 8 May 2013 (2013-05-08) cited in the application	13-15
A	paragraphs [0030], [0035] - [0047], [0049] - [0060]; figures 6,7	1-12

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/059807

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 2010120964 A2	21-10-2010	NONE	
EP 2204349 A1	07-07-2010	EP 2204349 A1	07-07-2010
		JP 5400602 B2	29-01-2014
		JP 2010162685 A	29-07-2010
		KR 20110028152 A	17-03-2011
		US 2010167078 A1	01-07-2010
EP 2554724 A9	08-05-2013	EP 2554724 A1	06-02-2013
		JP 5654115 B2	14-01-2015
		JP 2013527883 A	04-07-2013
		US 2013089485 A1	11-04-2013
		WO 2011120420 A1	06-10-2011